CLAIMS

- A dense cleaning fluid for removing contaminants from a substrate, the dense cleaning fluid comprising:
 - a dense fluid; and

at least one acetylenic alcohol or acetylenic diol represented by the following formulas (A) or (B):

$$\begin{array}{c}
R_1 - C - \longrightarrow H \\
O \\
R_2
\end{array}$$

Formula A

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Formula B

wherein R, R₁, R₃, and R₄ are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 34 carbon atoms, a branched alkyl group comprised of from 2 to 34 carbon atoms, and R₂ and R₅ are each independently a hydrogen atom; a hydroxyl terminated poly(alkylene oxide) chain derived from 1 to 30 alkylene oxide monomer units of the following formula (C):

Formula C

wherein R₆, R₇, R₈, and R₉ are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 5 carbon atoms, a branched alkyl group comprised of from 2 to 5 carbon atoms, or a cyclic alkyl group comprised of from 3 to 5 carbon atoms; an interactive functional group; and combinations thereof.

- 2. The dense cleaning fluid of Claim 1 further comprising at least one processing agent selected from the group consisting of a co-solvent, a surfactant, a chelating agent, and combinations thereof.
- 3. The dense cleaning fluid of Claim 2 wherein the co-solvent is selected from the group consisting of an ester, an ether, an alcohol, a nitrile, a hydrated nitrile, a glycol, a monester glycol, a ketone, a fluorinated ketone, a tertiary amine, an alkanolamine, an

amide, a carbonate, a carboxylic acid, an alkane diol, an alkane, a peroxide, a water, an urea, a haloalkane, a haloalkene, and combinations thereof.

- The dense cleaning fluid of Claim 3 wherein the cosolvent is a nitrile selected from the group consisting of benzonitrile, propiononitrile, acetonitrile, and combinations thereof.
 - 5. The dense cleaning fluid of Claim 2 wherein the chelating agent is selected from the group consisting of a beta-diketone, a carboxylic acid, an oxine, a tertiary amine, a tertiary diamine, a tertiary triamine, a nitrile, a beta-ketoimine, an ethylenediamine tetraacetic acid and derivatives thereof, a catechol, a choline-containing compound, a trifluoroacetic anhydride, an oxime, a dithiocarbamate, and combinations thereof.

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- 6. The dense cleaning fluid of Claim 1 wherein the interactive functional group is at least one selected from the group consisting of an amine and acid functional group; an ester functional group; an ether and alcohol functional group; an eitrile functional group; and a carbonate functional group.
- The dense cleaning fluid of Claim 1 wherein the dense fluid comprises one or more components selected from the group consisting of carbon dioxide, nitrogen, methane, oxygen, ozone, argon, hydrogen, helium, ammonia, nitrous oxide, hydrogen fluoride, hydrogen chloride, sulfur trioxide, sulfur hexafluoride, nitrogen trifluoride, monofluoromethane, difluoromethane, trifluoromethane, trifluoroethane, tetrafluoroethane, pentafluoroethane, pentafluoropropane, hexafluorobutadiene, octafluorocyclobutane, and methyl fluoride.
 - 8. The dense cleaning fluid of Claim 7 wherein the dense fluid comprises carbon dioxide.
 - 9. The dense cleaning fluid of Claim 1 wherein the dense fluid comprises at least one fluorinated dense fluid selected from perfluorocarbon compounds, hydrofluorocarbons, fluorine-containing compounds, fluorinated nitriles, fluoroethers, fluoroamines, fluorinated gases, and combinations thereof.

- 10. The dense cleaning fluid of Claim 1 wherein the contaminants are at least one selected from the group consisting of organic compounds, inorganic compounds, particulate matter, metal containing compounds, metal ions, and combinations thereof.
- 11. The dense cleaning fluid of Claim 1 wherein the substrate is at least one selected from a group comprising of a semiconductor, a semiconductor oxide, a metal, a dielectric, an organic polymer, a silicon or gallium arsenide wafer, a reticle, a photomask, a flat panel display, an internal surface of a processing chamber, surface mounted assemblies, electronic assemblies, electro-optical hardware, laser hardware, spacecraft hardware, surface micro-machined systems, and combinations thereof.
- 15 12. A dense cleaning fluid for removing contaminants from a substrate, the dense cleaning fluid comprising:

a dense fluid,

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at least one acetylenic alcohol or acetylenic diol represented by the following formulas (A) or (B):

$$R_1 - C - H$$
 $R_1 - C - R_4$
 R_2
 R_2
 R_3
 R_4
 R_5

Formula A

Formula B

wherein R, R_1 , R_3 , and R_4 are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 34 carbon atoms, a branched alkyl group comprised of from 2 to 34 carbon atoms, and R_2 and R_5 are each independently a hydrogen atom; a hydroxyl terminated poly(alkylene oxide) chain derived from 1 to 30 alkylene oxide monomer units of the following formula (C):

Formula C

wherein R_6 , R_7 , R_8 , and R_9 are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 5 carbon atoms, a branched alkyl group comprised of from 2 to 5 carbon atoms, or a cyclic alkyl group comprised of from 3 to 5 carbon atoms; an interactive functional group; and combinations thereof; and

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at least one processing agent selected from the group consisting of a co-solvent, a surfactant, a chelating agent, and combinations thereof.

13. The dense cleaning fluid of Claim 12 wherein the at least one co-solvent is selected from the group consisting of an ester, an ether, an alcohol, a nitrile, a hydrated nitrile, a glycol, a monester glycol, a ketone, a fluorinated ketone, a tertiary amine, an alkanolamine, an amide, a carbonate, a carboxylic acid, an alkane diol, an alkane, a peroxide, a water, an urea, a haloalkane, a haloalkene, and combinations thereof.

14. The dense cleaning fluid of Claim 13 wherein the at least one co-solvent is a nitrile selected from the group consisting of benzonitrile, propiononitrile, acetonitrile, and combinations thereof.

20 15. The dense cleaning fluid of Claim 12 wherein the chelating agent is selected from the group consisting of a beta-diketone, a carboxylic acid, an oxine, a tertiary amine, a tertiary triamine, a nitrile, a beta-ketoimine, an ethylenediamine tetraacetic acid and derivatives thereof, a catechol, a choline-containing compound, a trifluoroacetic anhydride, an oxime, a dithiocarbamate, and combinations thereof.

16. The dense cleaning fluid of Claim 12 wherein the dense fluid comprises one or more components selected from the group consisting of carbon dioxide, nitrogen, methane, oxygen, ozone, argon, hydrogen, helium, ammonia, nitrous oxide, hydrogen fluoride, hydrogen chloride, sulfur trioxide, sulfur hexafluoride, nitrogen trifluoride, monofluoromethane, difluoromethane, trifluoromethane, trifluoroethane, tetrafluoroethane, pentafluoroethane, pentafluoropropane,

hexafluoroethane, hexafluoropropylene, hexafluorobutadiene, octafluorocyclobutane, and methyl fluoride.

- 17. The dense cleaning fluid of Claim 12 wherein the interactive functional group is at least one selected from the group consisting of an amine and acid functional group; an ester functional group; an ether and alcohol functional group; an eiter and alcohol functional group; a nitrile functional group; and a carbonate functional group.
- 18. The dense cleaning fluid of Claim 12 wherein the contaminants are at least one
 selected from the group consisting of organic compounds, inorganic compounds, particulate matter, metal containing compounds, metal ions, and combinations thereof.
- 19. The dense cleaning fluid of Claim 12 wherein the substrate is at least one selected from a group consisting of a semiconductor, a semiconductor oxide, a metal, a dielectric, an organic polymer, a silicon or gallium arsenide wafer, a reticle, a photomask, a flat panel display, an internal surface of a processing chamber, surface mounted assemblies, electronic assemblies, electro-optical, laser, and spacecraft hardware, surface micro-machined systems, and combinations thereof.

20. A dense cleaning fluid for removing contaminants from a substrate, the dense cleaning fluid comprising:

20 to 99 weight percent of a dense fluid;

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1 to 20 weight percent of at least one acetylenic diol or acetylenic alcohol represented by the following formulas (A) or (B):

Formula A Formula B

wherein R, R₁, R₃, and R₄ are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 34 carbon atoms, a branched alkyl group comprised of from 2

to 34 carbon atoms, and R₂ and R₅ are each independently a hydrogen atom; a hydroxyl terminated poly(alkylene oxide) chain derived from 1 to 30 alkylene oxide monomer units of the following formula (C):

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Formula C

wherein R_6 , R_7 , R_8 , and R_9 are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 5 carbon atoms, a branched alkyl group comprised of from 2 to 5 carbon atoms, or a cyclic alkyl group comprised of from 3 to 5 carbon atoms; an interactive functional group; and combinations thereof;

0 to 40 weight percent of at least one cosolvent selected from the group consisting of an ester, an ether, an alcohol, a nitrile, a hydrated nitrile, a glycol, a monester glycol, a ketone, a fluorinated ketone, a tertiary amine, an alkanolamine, an amide, a carbonate, a carboxylic acid, an alkane diol, an alkane, a peroxide, a water, an urea, a haloalkane, a haloalkene, and combinations thereof; and,

0 to 20 weight percent of at least one chelating agent selected from the group consisting of a beta-diketone, a carboxylic acid, an oxine, a tertiary amine, a tertiary diamine, a tertiary triamine, a nitrile, a beta-ketoimine, an ethylenediamine tetraacetic acid and derivatives thereof, a catechol, a choline-containing compound, a trifluoroacetic anhydride, an oxime, a dithiocarbamate, and combinations thereof.

- 21. The dense cleaning fluid of Claim 20 wherein the dense fluid comprises carbon dioxide.
- 25 22. The dense cleaning fluid of Claim 20 wherein the dense fluid comprises at least one fluorinated dense fluid selected from perfluorocarbon compounds, hydrofluorocarbons, fluorinated nitriles, fluoroethers, fluoroamines, fluorinated gases, and combinations thereof.
- 30 23. The dense cleaning fluid of Claim 20 wherein the cosolvent comprises a nitrile selected from the group consisting of benzonitrile, propiononitrile, acetonitrile, and combinations thereof.

- 24. A dense cleaning fluid for removing contaminants from a substrate, the dense cleaning fluid comprising:
 - a dense fluid; and

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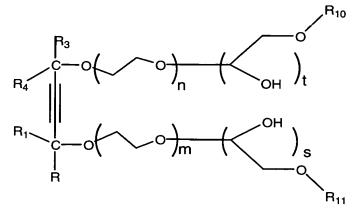
at least one derivatized acetylenic alcohol or a derivatized acetylenic diol wherein the derivatized alcohol or the derivatized diol comprises at least one interactive functional group selected from the group consisting of an amine and acid functional group; an ester functional group; an ether and alcohol functional group; an ester and alcohol functional group; a nitrile functional group; a carbonate functional group; and combinations thereof.

10 25. The dense cleaning fluid of Claim 24 wherein the derivatized acetylenic alcohol or the derivatized acetylenic diol is at least one member selected from the group consisting of compounds represented by Formulas (D) through (I):

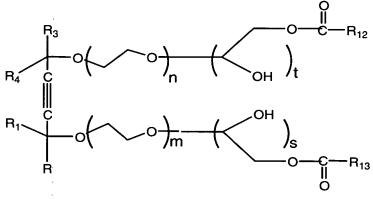
15 Formula D

$$\begin{array}{c|c}
R_{3} & O & O \\
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C & O & O \\
\hline
R_{1} & C & O \\
\hline
C & O & O \\
C & O & O \\
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Formula E



Formula F



Formula G

$$\begin{array}{c|c}
R_4 & C & C & C & C & C \\
\hline
R_1 & C & C & C & C & C
\end{array}$$

$$\begin{array}{c|c}
R_1 & C & C & C & C
\end{array}$$

Formula H

Formula I

wherein R, R₁, R₃, and R₄ are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 34 carbon atoms, or a branched alkyl group comprised of from 2 to 34 carbon atoms; R₁₀ and R₁₁ are each independently an alkyl group or a fluoroalkyl group comprised of from 1 to 34 carbon atoms; R₁₂, R₁₃, R₁₄, and R₁₅ are each independently an alkyl group comprised of from 1 to 34 carbon atoms; the value of m+n is a number ranging from 0 to 30 and the value of s+t is a number ranging from 1 to 2.

10 26. A method for removing contaminants from a substrate the method comprising contacting the substrate with a dense cleaning fluid comprising:

a dense fluid;

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at least one acetylenic alcohol or acetylenic diol represented by the following formulas (A) or (B):

Formula A

wherein R, R₁, R₃, and R₄ are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 34 carbon atoms, a branched alkyl group comprised of from 2 to 34 carbon atoms, and R₂ and R₅ are each independently a hydrogen atom; a hydroxyl terminated poly(alkylene oxide) chain derived from 1 to 30 alkylene oxide monomer units of the following formula (C):

Formula B

Formula C

wherein R_6 , R_7 , R_8 , and R_9 are independently a hydrogen atom, a linear alkyl group comprised of from 1 to 5 carbon atoms, a branched alkyl group comprised of from 2 to 5 carbon atoms, or a cyclic alkyl group comprised of from 3 to 5 carbon atoms; an interactive functional group; and combinations thereof.

- 27. The method of Claim 26 wherein the dense cleaning fluid further comprises at least one processing agent selected from the group consisting of a co-solvent, a surfactant, a chelating agent, and combinations thereof.
- 28. The method of Claim 27 wherein the contacting step is a dynamic method.
- 29. The method of Claim 27 wherein the contacting step is a static method.

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30. A method for removing contaminants from a substrate, the method comprising: introducing the substrate comprising contaminants into a processing chamber;

contacting the substrate with a dense cleaning fluid comprising a dense fluid and at least one processing agent selected from the group consisting of an acetylenic alcohol, an acetylenic diol, a derivatized acetylenic alcohol, a derivatized acetylenic diol, a cosolvent, a chelating agent, a surfactant, and combinations thereof to provide a spent dense fluid and a treated substrate; and

separating the contaminants and the at least one processing agent from the spent dense fluid.

- 31. The method of Claim 30 further comprising introducing ultrasonic energy into the processing chamber during at least a portion of the contacting step.
- 30 32. The method of Claim 30 wherein a pressure of the contacting step ranges from 1000 to 8000 psig.

- 33. The method of Claim 30 wherein a temperature of the contacting step ranges from 10 to 100°C.
- 34. A method for removing contaminants from a substrate, the method comprising: introducing the substrate comprising contaminants into a processing chamber;

combining a dense fluid, at least one fluorinated dense fluid, and at least one processing agent to provide a dense cleaning fluid;

contacting the substrate with the dense cleaning fluid to provide a spent dense cleaning fluid and a treated substrate;

separating the contaminants and the at least one processing agent from the spent dense cleaning fluid; and

separating at least one fluorinated dense fluid from the spent dense cleaning fluid wherein the at least one fluorinated dense fluid is purified to provide a purified fluorinated dense fluid and wherein at least a portion of the at least one fluorinated dense fluid in the combining step comprises the purified fluorinated dense fluid.

- 35. The method of claim 34 further comprising depressurizing and/or heating the spent dense fluid to transform the spent dense fluid into a gaseous phase.
- 36. The method of claim 34 wherein a pressure of the contacting step ranges from 500 to 4000 psig.
- 37. The method of claim 34 wherein a temperature of the contacting step ranges from 35 to 100°C.
 - 38. The method of claim 34 wherein the first separating step is conducted using at least one method selected from filtration, sedimentation, inertial separation, electrostatic precipitation, acoustic precipitation, condensation, thermal gradients, magnetic separation, flashing and combinations thereof.

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